Resonator-induced dissipation of transverse nuclear-spin signals in cold nanoscale samples

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The back action of typical macroscopic resonators used for detecting nuclear magnetic resonance can cause a reversible decay of the signal, known as radiation damping. A mechanical resonator that is strongly coupled to a microscopic sample can in addition induce an irreversible dissipation of the nuclear-spin signal, distinct from radiation damping. We provide a theoretical description of resonator-induced transverse relaxation that is valid for samples of a few nuclear spins in the low-temperature regime, where quantum fluctuations play a significant role in the relaxation process, as well as for larger samples and at higher temperatures. Transverse relaxation during free evolution and during spin locking are analyzed, and simulations of relaxation in example systems are presented. In the case where an isolated spin $\frac{1}{2}$ interacts with the resonator, transverse relaxation is exponential during free evolution, and the time constant for the relaxation is $T_2 = 2/R_h$, where R_h is the rate constant governing the exchange of quanta between the resonator and the spin. For a system of multiple spins, the time scale of transverse relaxation during free evolution depends on the spin Hamiltonian, which can modify the relaxation process through the following effects: (1) changes in the structure of the spin-spin correlations present in the energy eigenstates, which affect the rates at which these states emit and absorb energy, (2) frequency shifts that modify emission and absorption rates within a degenerate manifold by splitting the energy degeneracy and thus suppressing the development of resonator-induced correlations within the manifold, and (3) frequency shifts that introduce a difference between the oscillation frequencies of single-quantum coherences ρ_{ab} and ρ_{cd} and average to zero the transfers between them. This averaging guarantees that the spin transitions responsible for the coupling between ρ_{ab} and ρ_{cd} cause irreversible loss of order rather than a reversible interconversion of the coherences. In systems of a few spins, transverse relaxation is accelerated by a dipolar Hamiltonian that is either the dominant term in the internal spin Hamiltonian or a weak perturbation to the chemical-shift Hamiltonian. A pure chemical-shift Hamiltonian yields exponential relaxation with $T_2 = 2/R_h$ in the case where the Larmor frequencies of the spins are distinct and sufficiently widely spaced. During spin locking with a nutation frequency fast enough to average the evolution under the internal spin Hamiltonian but not the interactions occurring during the correlation time of the resonator, relaxation of the spin-locked component is exponential with time constant $T_{1\rho} = 2/R_h$.

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I. INTRODUCTION

Over the past two decades, force-detected nuclear magnetic resonance has evolved from a proposal[1] into a collection of experimental methods for sensitive detection of microscale and nanoscale spin samples. Magnetic-resonance force microscopy (MRFM)[2,3] has been used to detect a single electron spin[4] and to image nuclear spins with a resolution of <10 nm.[5] MRFM allows for isotope selectivity,[6] as well as for chemical selectivity by means of double resonance.[7,8] Methods of combining nuclear-magnetic-resonance (NMR) spectroscopy with MRFM have been developed,[9,10] enabling spatially localized spectroscopy. Force-detected NMR spectroscopy without the use of field gradients has been demonstrated.[11]

In force-detected NMR, spatial and/or spectral information about a spin system is encoded into mechanical motion by means of a resonant force exerted on a mechanical oscillator by the spins. The mechanical frequency is typically orders of magnitude smaller than the Larmor frequency, and modulation of the spin dipole by means of radiofrequency (rf) fields is required in order to produce a resonant mechanical force. Since the spectral density of the noisy thermal force acting on an oscillator is proportional to its motional mass,[2] however, it is natural to consider using scaled-down low-mass oscillators for force detection. Scaling down an oscillator design typically causes the mechanical frequency to vary inversely with the length scale, and so the goal of decreasing motional mass has led to proposals for nanoscale force-detected NMR in which mechanical motion is resonant with spin precession at the Larmor frequency.[11–13]

In addition to functioning as a sensitive detector, a cold nanoscale resonator could be used to polarize nuclear spins by enhancing their spontaneous emission.[12,14] Spin relaxation due to spontaneous emission is typically too slow to be relevant for NMR experiments,[15] even when the spontaneous emission is enhanced by a macroscopic inductive resonator.[16,17] Due to the strong dependence of the spin-resonator coupling constant on length scale, however, spontaneous emission induced by a scaled-down mechanical resonator could in favorable cases be an efficient polarization method in the low-temperature limit where the spin polarization P is of order unity.[14] In particular, a calculation for a prototype resonator design suggests the possibility of resonator-induced polarization with a rate constant $\sim 1\ \mathrm{s}^{-1}$ in the low-temperature limit.[12] Note that at temperatures where the thermal number of quanta n_{th} in the resonator is $\gg 1$, spontaneous emission is weak in comparison to stimulated absorption and emission, which relaxes the spins toward $P = 0$.[14] Resonator-induced relaxation has been observed experimentally in this high-temperature regime, in an experiment where mechanical motion was resonant with Rabi nutation in an applied rf field.[18] In a reference frame rotating

at the instantaneous frequency of the rf field, the relaxing spin component was aligned with the axis of the effective field, and the relaxation process can be viewed as a form of longitudinal relaxation, analogous to the high-temperature limit of the proposed scheme for resonator-induced polarization.[14]

A strong spin-resonator coupling that allows for sensitive detection of nanoscale samples also allows for resonator-induced decay of the transverse spin components during transients. A well-known example of such decay, observable with macroscopic inductive resonators, is so-called radiation damping,[19] that is, rotation of the spin dipole into alignment with the static field due to the back action of the resonator. Unlike radiation damping, which does not involve dissipation,[19] spin transitions stimulated by quantum and thermal fluctuations cause irreversible transverse relaxation. At low temperatures, where lattice fluctuations are "frozen out," fluctuating spin-resonator interactions can become the dominant source of relaxation, including cooling of the spins[14] and dissipation of precessing transients. An understanding of resonator-induced transverse relaxation is thus important for the development of methods in which a cold nanoscale resonator is coupled to transverse spin components, for example, during spin locking.[12] More generally, the experimental observation of longitudinal relaxation induced by a microscale resonator in the high-temperature regime[18] suggests that the contribution of a strongly coupled resonator to transverse relaxation could be detectable under a variety of experimental conditions.

Our concern here is to provide a description of resonator-induced transverse relaxation that is valid for nanoscale samples in the low-temperature regime, where quantum fluctuations play a significant role in the relaxation process, as well as for larger samples and at higher temperatures. The theoretical framework developed in Ref. 14 for the study of resonator-induced polarization is extended to the problem of transverse relaxation. Section II analyzes the equations of motion that govern transverse relaxation during free evolution under the secular spin Hamiltonian and during continuous spin locking by a resonant rf field. In the case where an isolated spin $\frac{1}{2}$ interacts with the resonator, transverse relaxation is exponential during free evolution, and the time constant $T_2 = 2/R_h$ is determined by the lifetimes of the two spin states in the presence of the fluctuating spin-resonator interactions. (Here R_h is the rate constant for resonator-induced longitudinal relaxation of a single spin $\frac{1}{2}$ due to spontaneous and stimulated spin transitions.[14]) In a system of multiple spins, the eigenstate lifetimes do not in general determine the time scale of transverse relaxation during free evolution, since spin transitions can cause a modification of spin order rather than an irreversible loss of order. The spin Hamiltonian can modify the relaxation process through the following effects:

(1) changes in the structure of the spin-spin correlations present in the energy eigenstates, which affect the rates at which the states emit and absorb energy,[14]

(2) frequency shifts that modify emission and absorption rates within a degenerate manifold by splitting the energy degeneracy and thus suppressing the development of resonator-induced correlations within the manifold, and

(3) frequency shifts that introduce a difference between the oscillation frequencies of single-quantum coherences ρ_{ab} and ρ_{cd}, with $a \neq c$ and $b \neq d$, and average to zero the transfers between them.

This averaging guarantees that the spin transitions responsible for the coupling between ρ_{ab} and ρ_{cd} cause irreversible loss of order rather than a reversible interconversion of the coherences. The form of the master equation that governs the density matrix during spin locking depends on the magnitude of the nutation frequency ω_1 relative to the bandwidth of the mechanical fluctuations. For a broad-bandwidth resonator, the interactions occurring during the resonator's correlation time are unaffected by the rf field, but the resulting spin transitions are modulated by the nutation of the spin system. If the nutation is fast enough to average the internal spin Hamiltonian, relaxation of the spin-locked component is exponential with time constant $T_{1\rho} = 2/R_h$, the same time constant obtained for the transverse relaxation of a freely precessing spin $\frac{1}{2}$. In the limiting case of strong spin locking, the nutation of the spins is fast enough to average the interactions occurring during the resonator's correlation time, and no relaxation of the spin-locked component is induced by the resonator.

Section III analyzes the relaxation of two-spin example systems and presents simulations of systems containing up to five spins. Since spin angular momentum is conserved by the Hamiltonian H_1 that governs the spin-resonator interaction, the spin transitions induced by the resonator are between correlated angular-momentum eigenstates,[14,20] unless the spin Hamiltonian breaks this symmetry. In a system of isochronous spins that interact only with the resonator, these transitions modify the spin-spin correlations present in the system and can be considered to select angular-momentum eigenstates to participate in coherences. In a two-spin system, a sufficiently strong dipolar Hamiltonian H_D accelerates the relaxation of these coherences by means of frequency shifts that average to zero the reversible transfers between them. Simulations of dipolar-coupled systems of three, four, and five spins also show accelerated transverse relaxation due to H_D. In the absence of a dipolar coupling between the spins, the transverse relaxation of the two-spin system is slowed by a sufficiently strong chemical-shift Hamiltonian H_{CS}. The development of resonator-induced correlations is suppressed, since product states rather than angular-momentum eigenstates participate in transitions. In addition, H_{CS} decouples coherences involving a flip of spin 1 from those involving a flip of spin 2, so that each set of coherences relaxes independently. As a result, transverse relaxation is exponential with time constant $T_2 = 2/R_h$. The Appendix shows that this result can be generalized to N-spin systems in which H_{CS} decouples product-state coherences involving a flip of spin i from those involving a flip of spin j, for all $i \neq j$. Under these conditions, however, a dipolar coupling $H_D \ll H_{CS}$ that does not significantly perturb the eigenstates can suppress the reversible interconversion of coherences essential for this slow exponential relaxation and cause accelerated transverse relaxation. This effect is illustrated by simulation of a four-spin system in which H_D causes fast transverse relaxation without affecting the longitudinal relaxation. Simulations of spin locking in systems governed by H_D and $H_D + H_{CS}$ show that the dissipation of

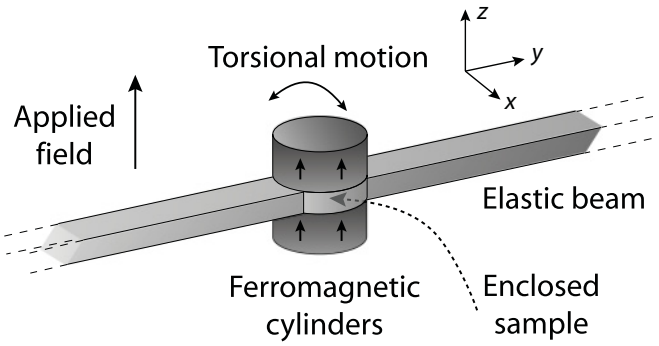

FIG. 1. Prototypical resonator design proposed in Ref. 12 for NMR spectroscopy of nanoscale samples. The sample is "sandwiched" between magnetic cylinders and rotates with the sandwich about the torsional beam. The spin dipole couples to the oscillating transverse field generated by the cylinders.

the spin-locked component is substantially slower than the transverse relaxation in the freely evolving system, even in cases where the largest dipolar couplings are within a factor of 2 of the nutation frequency ω_1.

The simulation methods used for this paper are described in Sec. IV.

II. EQUATIONS OF MOTION

Figure 1 shows a prototypical torsional resonator design proposed in Ref. 12 for use in NMR spectroscopy of nanoscale samples. We will use this resonator design for purposes of visualization, but the formalism that describes the spin-resonator system is not substantially altered if the torsional resonator used here as an example is replaced with a translational mechanical resonator or an inductive resonator.[14] The figure shows a "magnetic sandwich" that consists of two ferromagnetic cylinders and a disk of silicon that separates them, with the sample placed in a hollow space in the center of the silicon disk. The sandwich encloses an elastic beam, and the beam and sandwich together undergo torsional oscillations about the beam's long axis, labeled as the y axis in the figure. The structure consisting of the sandwich and the beam is a torsional mechanical resonator with fundamental frequency ω_h and coordinate θ, defined as the angular displacement of the sandwich axis from the z axis. Since the motion of the ferromagnetic cylinders modulates the magnetic field $\mathbf{B}(\theta)$ at the spins, the resonator is coupled to the spins.

A. Interaction-frame master equation

For a system of isochronous spins that interact only with the resonator and have the identical couplings to it, the Hamiltonian can be written as

$$H = H_0 + H_1,$$

where

$$H_0 = \omega_0 I_z + \omega_h (a^\dagger a + 1) \tag{1}$$

governs the fast, unperturbed motion of the spins and the resonator and where the interaction Hamiltonian that survives averaging by H_0 is[14]

$$H_1 = g(I_+ a^\dagger + I_- a). \tag{2}$$

In Eq. (1), the spin component I_z is summed over all the spins, and $\omega_0 = -\gamma B_0$ is the Larmor frequency, with γ the gyromagnetic ratio and B_0 the time-averaged field at the spins; $a^\dagger$ and a, respectively, represent the raising operator and the lowering operator for the mechanical oscillator. In Eq. (2), I_+ and I_-, respectively, represent the raising operator and lowering operator summed over all the spins, and

$$g = \frac{-\gamma}{2}\sqrt{\frac{\hbar}{2 I_h \omega_h}}\frac{dB_x}{d\theta} \tag{3}$$

is the coupling constant for the resonant interaction, with I_h the resonator's moment of inertia. Equation (2) depends on the assumption that the mechanical frequency is resonant with the Larmor frequency. We have also assumed that $\gamma > 0$ and that the time-averaged field at the spins points along the positive z axis, which together give $\omega_0 < 0$. The resonance condition can thus be written as $\omega_h = -\omega_0$.

In the regime where the resonator's correlation time is short compared to the time required for transfer of quanta between the spins and the resonator under H_1, the resonator acts as a thermal bath that damps the spin motion, and the evolution of the spin density matrix ρ is governed by a reduced master equation that does not explicitly include the resonator's degrees of freedom.[21,22] If the bandwidth of the resonator fluctuations is broad compared to the spectral width of the rotating-frame spin Hamiltonian $H_{\rm spin}$, the reduced master equation for a system of spins that have identical couplings to the resonator is[14,21]

$$\frac{d\rho}{dt} = -i[H_{\rm spin}, \rho] + \Lambda\rho. \tag{4}$$

In Eq. (4), the spin-relaxation superoperator Λ is given by

$$\begin{aligned}\Lambda\rho = {} & R_0(n_{\rm th}+1)\left(I_+\rho I_- - \tfrac{1}{2}[I_- I_+, \rho]_+\right) \\ & + R_0 n_{\rm th}\left(I_-\rho I_+ - \tfrac{1}{2}[I_+ I_-, \rho]_+\right),\end{aligned} \tag{5}$$

where

$$R_0 = 2g^2\tau_h, \tag{6}$$

and where τ_h is the time constant for decay of the mechanical displacement in the absence of coupling to the spins. Equations (4) and (5) hold in the rotating frame where the term $\omega_0 I_z$ has been eliminated from the spin Hamiltonian. In these equations, ρ represents the rotating-frame density matrix, while I_+, I_-, and $H_{\rm spin}$ are time-independent operators. In Eq. (5), $n_{\rm th}$ is the thermal number of quanta in the resonator. Note that R_0 can be interpreted as the rate constant for spontaneous emission by the spins into the resonant mode.[14] For the prototype resonator design of Ref. 12, numerical estimates predict

$$R_0 \approx 1\ \mathrm{s}^{-1}.$$

In studying the relaxation of transverse spin components, it is natural to transform the reduced master equation to

an interaction frame where H_{spin} has been eliminated. This transformation yields

$$\frac{d\tilde{\rho}}{dt} = \tilde{\Lambda}\tilde{\rho}, \tag{7}$$

where $\tilde{\Lambda}\tilde{\rho}$ is obtained from Eq. (5) by replacing each operator A appearing on the right side of (5) by

$$\tilde{A} = \exp(itH_{\text{spin}})A\exp(-itH_{\text{spin}}). \tag{8}$$

In particular, note that the operator $\tilde{\rho}$ obtained in this way from ρ is the interaction-frame density matrix. [Throughout this paper, a tilde over an operator or superoperator indicates that it has been transformed into the reference frame defined by Eq. (8).]

B. Equation of motion for transverse relaxation

Equation (7) can be used to obtain interaction-frame relaxation equations for $\langle I_x\rangle$ and $\langle I_y\rangle$ in the low-temperature regime where lattice fluctuations are "frozen out" and where the spin-resonator interaction becomes the dominant relaxation mechanism. Letting I_u denote either of the time-independent operators I_x, I_y, we have

$$\frac{d}{dt}\langle I_u\rangle = R_0(n_{\text{th}}+1)\left\langle \tilde{I}_- I_u \tilde{I}_+ - \frac{1}{2}[I_u, \tilde{I}_-\tilde{I}_+]_+\right\rangle + R_0 n_{\text{th}}\left\langle \tilde{I}_+ I_u \tilde{I}_- - \frac{1}{2}[I_u, \tilde{I}_+\tilde{I}_-]_+\right\rangle. \tag{9}$$

Equation (9) does not in general lend itself to simplification, since the commutators $[I_u,\tilde{I}_x]$ and $[I_u,\tilde{I}_y]$ depend on the evolution operators $\exp(\pm itH_{\text{spin}})$. Partly because of the difficulty of simplifying this equation, our study of transverse relaxation will be mainly based on analysis of the matrix elements of the master equation (7). In the case where the spin system consists of a single spin $\frac{1}{2}$, however, Eq. (9) simplifies to

$$\frac{d}{dt}\langle I_u\rangle = -\frac{1}{2}R_h\langle I_u\rangle, \tag{10}$$

where

$$R_h = R_0(2n_{\text{th}}+1). \tag{11}$$

The resonator thus induces exponential transverse relaxation governed by the time constant

$$T_2 = 2/R_h. \tag{12}$$

Note that the corresponding time constant for longitudinal relaxation of a single spin $\frac{1}{2}$ is[14]

$$T_1 = 1/R_h.$$

An alternative simplification of Eq. (9) is possible if $H_{\text{spin}} = 0$:

$$\frac{d}{dt}\langle I_u\rangle = -\frac{1}{2}R_h\langle I_u\rangle - \frac{1}{2}R_0\langle I_u I_z + I_z I_u\rangle. \tag{13}$$

The well-known phenomenon of radiation damping[19] can be described using Eq. (13). Since the thermal fluctuations of the resonator do not play an essential role in radiation damping, we demonstrate this by considering an example where the resonator is at temperature 0 K. Suppose that a large number of spins are aligned in the xz plane, with

$$\tfrac{1}{2}\langle I_x I_z + I_z I_x\rangle \approx \langle I_x\rangle\langle I_z\rangle \gg \langle I_x\rangle.$$

Since $n_{\text{th}} = 0$, Eq. (13) gives

$$\frac{d}{dt}\langle I_x\rangle \approx -R_0\langle I_x\rangle\langle I_z\rangle. \tag{14}$$

It is straightforward to verify that Eq. (14) is the equation of motion for $\langle I_x\rangle$ in the case where the spin dipole rotates away from the x axis and toward the z axis due to the back action of the resonator. Indeed, Abragam's equation of motion for radiation damping[23] can be obtained from (14) if $R_0 = 2g^2\tau_h$ is replaced with the corresponding constant $2g_L^2\tau_L$ for an inductive resonator,[14] where the inductive coupling constant g_L is

$$g_L = -\frac{\gamma}{2}\frac{\mu_0 n}{L}\sqrt{\frac{L\hbar\omega_L}{2}}, \tag{15}$$

and where the ring-down time of the inductive circuit is

$$\tau_L = 2L/R. \tag{16}$$

In Eq. (15), n is the number of turns per unit length of the long solenoid generating the field, L is the circuit inductance, and ω_L is the resonant frequency of the inductive circuit. In Eq. (16), R represents the circuit resistance.

C. Effect of the spin Hamiltonian and the indirect spin-spin interaction

The process of radiation damping is reversible and is not properly considered a form of damping.[23] However, a strongly coupled resonator can also induce fast, irreversible transverse relaxation in systems containing multiple spins; in particular, the dipolar Hamiltonian can accelerate the process of resonator-induced relaxation, as we show in Sec. III. In analyzing the way in which H_{spin} affects transverse relaxation, we find it convenient to express the matrix elements of Eq. (7) using a basis set of energy eigenstates. Let S denote the spin system and R the reservoir that damps the spins, that is, the resonator and its thermal bath. The sets $\{|a\rangle\}$, $\{|\mu\rangle\}$ represent orthonormal bases of energy eigenfunctions for S and R, respectively; the product states $|a\rangle|\mu\rangle$ would be energy eigenstates in the absence of the spin-resonator coupling. The energy (in rad/s) of a state $|a\rangle$ is denoted by ω_a, and the Bohr frequencies of S by $\omega_{ab} = \omega_a - \omega_b$. Equation (7), the interaction-frame master equation, can be written as[24]

$$\frac{d}{dt}\tilde{\rho}_{ab}(t) = \sum_{c,d}\exp[i(\omega_{ab}-\omega_{cd})t]\mathcal{R}_{abcd}\,\tilde{\rho}_{cd}(t). \tag{17}$$

The coefficients $\mathcal{R}_{abcd}$ are constants obtained by calculating the matrix elements of the relaxation superoperator Λ of Eq. (5) in the Liouville-space basis set $\{|a\rangle\langle b|\}$, where the kets $|a\rangle$ and bras $\langle b|$ each range over the set of spin-energy eigenstates.

As discussed in Ref. 14, terms in the spin Hamiltonian can affect Eq. (17) in two distinct ways: (1) by modifying the coefficients $\mathcal{R}_{abcd}$ and (2) by shifting the frequencies $(\omega_{ab}-\omega_{cd})$. A perturbation in H_{spin} which does not significantly change the energy eigenstates will not affect the coefficients $\mathcal{R}_{abcd}$. In particular, consider the case where the spin Hamiltonian

contains two noncommuting terms H' and H'', with $H' \gg H''$. The spin-energy eigenstates can be approximated as those of H', with any degenerate eigenstates of H' chosen to be zero-order eigenstates of the weak perturbation H''. Since "turning on" H'' cannot significantly affect the coefficients $\mathcal{R}_{abcd}$, the weak perturbation can contribute to the relaxation only by shifting $(\omega_{ab} - \omega_{cd})$, the frequency at which the relative phase of laboratory-frame coherences ρ_{ab} and ρ_{cd} is modulated by the spin Hamiltonian. This laboratory-frame modulation in relative phase appears in the interaction frame as an oscillation in the phase of the coupling between $\tilde{\rho}_{cd}$ and $\tilde{\rho}_{ab}$, due to the presence of the factor $\exp[i(\omega_{ab} - \omega_{cd})t]$ in Eq. (17). As an example of the effect of such a perturbation, note that if the frequency difference $|\omega_{ab} - \omega_{cd}|/2\pi \ll |\mathcal{R}_{abcd}|$ is perturbed to a value much larger than $|\mathcal{R}_{abcd}|$, then the relaxation associated with transfer from $\tilde{\rho}_{cd}$ to $\tilde{\rho}_{ab}$ will be suppressed, since H'' will average the net transfer to zero.

The coefficients $\mathcal{R}_{abcd}$ are determined by the rates at which spin transitions are induced by the resonator. In quantifying the way in which spin transitions cause transverse relaxation, we follow Ref. 24 in introducing the notation

$$\Gamma_{a\to b} \equiv \mathcal{R}_{bbaa} \tag{18}$$

for the rate constant governing transfer from population $\tilde{\rho}_{aa}$ to $\tilde{\rho}_{bb}$. Note that $\Gamma_{a\to b}$ can be interpreted as the probability per unit time that a state from the manifold $\{|\mu,a\rangle\}$ makes the transition to the manifold $\{|\nu,b\rangle\}$, where a and b are fixed, while μ, ν range over the orthonormal basis of R.[24] If a coherence $\tilde{\rho}_{ab}$ is not coupled to any population or to any other coherence by Eq. (17), the rate constant for its decay due to resonator-induced transitions is[24]

$$|\mathcal{R}_{abab}| = \frac{1}{2}\left(\sum_{n\neq a}\Gamma_{a\to n} + \sum_{n\neq b}\Gamma_{b\to n}\right). \tag{19}$$

The decay rate of an isolated coherence $\tilde{\rho}_{ab}$ is the average of the rates at which transitions are induced in the ket $|a\rangle$ and the bra $\langle b|$. Equation (19) can thus be interpreted as characterizing decay due to the finite lifetimes of the two states involved in the coherence.

By way of illustration, we note that the value of T_2 for a single spin $\frac{1}{2}$, given above by Eq. (12), can be obtained from Eq. (19). Let $|a\rangle = |+\rangle$ and $|b\rangle = |-\rangle$. From Eq. (5), it follows that

$$\Gamma_{a\to b} = R_0 n_{\rm th}, \tag{20a}$$

$$\Gamma_{b\to a} = R_0(n_{\rm th} + 1). \tag{20b}$$

The two coherences $\tilde{\rho}_{ab}$ and $\tilde{\rho}_{ba}$ each decay exponentially with rate constant

$$\tfrac{1}{2}(\Gamma_{a\to b} + \Gamma_{b\to a}) = \tfrac{1}{2}R_0(2n_{\rm th} + 1) \tag{21}$$

and the decay of $\langle I_x\rangle = (\tilde{\rho}_{ab} + \tilde{\rho}_{ba})/2$ is governed by the same rate constant. The rate of transverse relaxation is fully determined by the lifetimes of the states $|a\rangle$ and $|b\rangle$.

In general, however, the rate constants $|\mathcal{R}_{abab}|$ that would govern the decay of isolated coherences are not sufficient to characterize transverse relaxation, since Eq. (17) includes couplings between coherences. Examination of the rotating-frame relaxation superoperator given by Eq. (5) shows that there are two distinct mechanisms by which spin transitions couple single-quantum coherences. The first mechanism is associated with the terms $I_+\rho I_-$ and $I_-\rho I_+$, which convert $|a\rangle\langle b|$ to $|c\rangle\langle d|$ by means of two single-quantum transitions $|a\rangle \to |c\rangle$ and $\langle b| \to \langle d|$. Although these transitions destroy the coherence $\tilde{\rho}_{ab}$ and thus contribute to $|\mathcal{R}_{abab}|$, they do not necessarily cause a loss of spin order, since the coherence $\tilde{\rho}_{cd}$ may be strengthened by the transition $|a\rangle\langle b| \to |c\rangle\langle d|$. Note that frequency shifts associated with perturbations to the spin Hamiltonian can play a significant role in determining whether the transitions $|a\rangle\langle b| \leftrightarrow |c\rangle\langle d|$ result in a reversible interconversion of the coherences $\tilde{\rho}_{ab}$ and $\tilde{\rho}_{cd}$ or an irreversible loss of spin order. In particular, if

$$|\omega_{ab} - \omega_{cd}|/2\pi \gg |\mathcal{R}_{abcd}|, |\mathcal{R}_{cdab}|,$$

then Eq. (17) implies that the interconversion of $\tilde{\rho}_{cd}$ and $\tilde{\rho}_{ab}$ is averaged to zero, due to the quickly oscillating phase of the coupling. Under these circumstances, the transitions $|a\rangle\langle b| \leftrightarrow |c\rangle\langle d|$ will be associated with irreversible loss of spin order. A perturbation that shifts $|\omega_{cd} - \omega_{ab}|/2\pi$ sufficiently far from zero will guarantee this loss of spin order.

The second mechanism by which single-quantum coherences are coupled is associated with the terms $[I_-I_+,\rho]_+$ and $[I_+I_-,\rho]_+$ in Eq. (5). These terms cause either a ket or a bra to make a second-order transition that involves a transitory intermediate state.[14] For example, the conversion of $|a\rangle\langle b|$ to $|c\rangle\langle b|$ depends on a second-order transition $|a\rangle \to |n\rangle \to |c\rangle$, where $n \neq a,c$. Note that since resonator-induced relaxation is slow on the time scale of spin dynamics, a coupling between $\tilde{\rho}_{ab}$ and $\tilde{\rho}_{cb}$ can only affect the evolution if the frequencies of these coherences are approximately equal, that is, if $|a\rangle$ and $|c\rangle$ are essentially degenerate. [From Eq. (17), the coupling between the coherences is averaged to zero unless $\omega_{ab} \approx \omega_{cb}$.] In this case, we can interpret the second-order transition $|a\rangle \to |n\rangle \to |c\rangle$ as changing the nature of the ket involved in the coherence. If the transfer of probability amplitude from $|a\rangle$ to $|c\rangle$ converts $|a\rangle$ into the linear combination $(u_1|a\rangle + u_2|c\rangle)$, then $|a\rangle\langle b|$ is converted to $(u_1|a\rangle + u_2|c\rangle)\langle b|$. The spin-resonator interaction can thus select certain linear combinations of degenerate states to participate in coherences. In a system of isochronous spins that interact only with the resonator, for instance, spin angular momentum is conserved by the interaction Hamiltonian H_1, and so the transitions induced by the resonator are between angular-momentum eigenstates $|I,M\rangle$, where I is the total angular momentum and M is the z component.[14,20] These transitions modify the spin-spin correlations present within degenerate manifolds having the same I_z eigenvalue, and it is natural to view the transitions as selecting the states $|I,M\rangle$ from within these manifolds to be the energy eigenstates that are involved in coherences. More generally, when a degenerate manifold of energy eigenstates exists, the symmetry of the spin-resonator interaction determines which linear combinations of these states emit and absorb energy, and it is these linear combinations that are most naturally considered to be involved in coherences. The mechanism by which these linear combinations are selected can be visualized in terms of an indirect spin-spin interaction that is present when multiple spins are coupled to a single resonator.[14] The indirect interaction can modify the states that are involved in coherences by inducing correlated spin motions within degenerate manifolds.

If the degeneracy is removed by frequency shifts associated with the spin Hamiltonian, it is the symmetry of H_{spin} rather than the symmetry of H_1 that determines which states emit and absorb energy. In general, the rate constants for spin transitions, and thus the rates at which coherences decay, will be modified by such frequency shifts. Within the formalism of the master equation, the contribution of resonator-induced correlations to transverse relaxation is suppressed if the frequencies $|\omega_{ab} - \omega_{cb}|/2\pi$ are shifted sufficiently far from zero:

$$|\omega_{ab} - \omega_{cb}|/2\pi \gg |\mathcal{R}_{abcb}|, |\mathcal{R}_{cbab}|.$$

In summary, the effects of the spin Hamiltonian and the indirect spin-spin interaction can be analyzed by considering two factors that affect the transverse relaxation rate: (1) the magnitudes of the rate constants $\Gamma_{a\to n}$ and $\Gamma_{b\to n}$ governing the spin transitions that destroy single-quantum coherences $\tilde{\rho}_{ab}$ and (2) the extent to which the transitions of the form $|a\rangle\langle b| \leftrightarrow |c\rangle\langle d|$ cause an irreversible loss of spin order rather than reversible interconversion of coherences. The rate constants $\Gamma_{a\to n}$ and $\Gamma_{b\to n}$ are affected by perturbations to the spin Hamiltonian that are strong enough to significantly modify the spin-spin correlations present in the eigenstates,[14] or by the indirect spin-spin interaction, which selects particular linear combinations of degenerate eigenstates to be involved in coherences. Frequency shifts can suppress the effects of the indirect spin-spin interaction by splitting the energy degeneracy of a manifold and averaging to zero the transfers responsible for the development of resonator-induced correlations. Frequency shifts that suppress couplings between coherences $\tilde{\rho}_{ab}$ and $\tilde{\rho}_{cd}$, with $a \neq c$ and $b \neq d$, guarantee that the spin transitions responsible for the couplings cause irreversible loss of order.

D. Resonator-induced relaxation during spin locking

The contributions of the internal spin Hamiltonian and the indirect spin-spin interaction to transverse relaxation can be suppressed by spin locking, which has been proposed as a method of prolonging transients during detection by a mechanical resonator.[11,12] In obtaining equations of motion for resonator-induced relaxation during a continuous period of spin locking, we first consider the case where the only contribution to the rotating-frame spin Hamiltonian is due to the spin-locking field, which causes nutation at frequency ω_1 about the x axis:

$$H_{\text{spin}} = \omega_1 I_x.$$

In the regime where the bandwidth of the resonator fluctuations is large compared to ω_1, the spin-resonator interactions occurring during the correlation time of the resonator are unaffected by H_{spin}. During a time step $\Delta t \ll 2\pi/\omega_1$, the resulting spin transitions are governed by the superoperator Λ of Eq. (5). These transitions are modulated by the nutation of the spin system about the x axis. The spin transitions that survive averaging due to this modulation can be found by transforming Λ into the reference frame where the Hamiltonian for the applied rf field has been eliminated, commonly known as the toggling frame. Equation (8) can be used to obtain an explicit expression for the averaged superoperator, which we denote by Λ_1:

$$\Lambda_1\tilde{\rho} = R_h\left(I_x\tilde{\rho}I_x - \frac{1}{2}\left[I_x^2,\tilde{\rho}\right]_+\right) + \frac{R_h}{2}\left(I_y\tilde{\rho}I_y - \frac{1}{2}\left[I_y^2,\tilde{\rho}\right]_+\right) + \frac{R_h}{2}\left(I_z\tilde{\rho}I_z - \frac{1}{2}\left[I_z^2,\tilde{\rho}\right]_+\right). \quad (22)$$

[Note that in the case where the only term in the rotating-frame spin Hamiltonian is $\omega_1 I_x$, the toggling frame is equivalent to the interaction frame defined by Eq. (8), and so we use $\tilde{\rho}$ to denote the density matrix in this frame.] Formally, Eq. (22) is the relaxation superoperator associated with three statistically independent fields fluctuating along the three Cartesian axes of the toggling frame. Each field causes rotations of the spin system about a Cartesian axis. The resulting relaxation of spin components is exponential; for example, the equation of motion for the spin-locked component $\langle I_x\rangle$ is

$$\frac{d}{dt}\langle I_x\rangle = -\frac{R_h}{2}\langle I_x\rangle. \quad (23)$$

Note that the transitions occurring during the correlation time of the resonator are between correlated spin states belonging to the same angular-momentum manifold,[14] and while such transitions in general do not relax spins to thermal equilibrium,[14,20] averaging of these transitions due to nutation about the x axis yields a superoperator that can be interpreted as relaxing individual spins independently, since the Cartesian components of each spin relax exponentially, independent of the state of the other spins. The development of resonator-induced correlations is thus suppressed by the averaging process.

A simple analysis is also possible in the opposite regime, where ω_1 is large compared to the bandwidth of the mechanical fluctuations. In this regime, the nutation of the spins about the x axis is fast enough to average the spin-resonator interactions occurring during the correlation time of the resonator. The terms in the interaction Hamiltonian H_1 of Eq. (2) that survive averaging are those involving I_x, which is not modulated by the nutation about the rf field. As might be expected, the toggling-frame relaxation superoperator is

$$\Lambda_2\tilde{\rho} = R_h\left(I_x\tilde{\rho}I_x - \tfrac{1}{2}\left[I_x^2,\tilde{\rho}\right]_+\right); \quad (24)$$

that is, increasing the strength of the spin-locking field along the x axis modifies the superoperator of Eq. (22) by averaging to zero the effects of fluctuating fields along axes orthogonal to the x axis. As a result, the spin-resonator interaction does not cause relaxation of the spin-locked component:

$$\frac{d}{dt}\langle I_x\rangle = 0. \quad (25)$$

Note that Eq. (24) can be derived formally using Eq. (A1) of Ref. 14, which gives a general formula for the relaxation superoperator in terms of correlation functions involving $\tilde{I}_-(t)$ and $\tilde{I}_+(t)$. Substituting

$$\tilde{I}_\pm(t) = \{I_x \pm i[I_y\cos(\omega_1 t) - I_z\sin(\omega_1 t)]\}e^{\pm i\omega_0 t}$$

into this formula and evaluating the correlation functions under the assumption $|\omega_1| \gg 1/\tau_h$ yields Eq. (24).

Moving beyond the case in which the spin-locking field is the only term in the spin Hamiltonian, we consider systems for which

$$H_{\rm spin} = H_{\rm int} + \omega_1 I_x,$$

where $H_{\rm int}$ is the internal spin Hamiltonian that carries information about the microscopic environment of the nuclear spins. In the toggling frame, the internal spin Hamiltonian takes the form

$$H^*_{\rm int} = \exp(i\omega_1 I_x t) H_{\rm int} \exp(-i\omega_1 I_x t), \tag{26}$$

where an asterisk rather than a tilde has been used to distinguish the transformation of Eq. (26) from that of Eq. (8). In deriving relaxation equations, we first consider the case where the bandwidth of the resonator fluctuations is large compared to ω_1. Transforming the rotating-frame master equation of Eq. (4) into the toggling frame gives

$$\frac{d\rho^*}{dt} = -i[H^*_{\rm int}, \rho^*] + \Lambda^* \rho^*. \tag{27}$$

If nutation about the spin-locking field is sufficiently fast that the time-dependent terms $H^*_{\rm int}$ and Λ^* can be approximated by their time averages, then Eq. (27) simplifies to

$$\frac{d\rho^*}{dt} = -i[\bar{H}_{\rm int}, \rho^*] + \Lambda_1 \rho^*, \tag{28}$$

where $\bar{H}_{\rm int}$ represents the time average of $H^*_{\rm int}$. Note that in the regime where the spin-locking field is strong enough to average the internal Hamiltonian but not sufficiently strong to average the spin-resonator interactions occurring during the correlation time of the resonator, the equation of motion can be obtained by adding the commutator $-i[\bar{H}_{\rm int}, \cdot]$ to the relaxation superoperator Λ_1 derived under the assumption that $H_{\rm int} = 0$. Under these conditions, the commutator of makes no contribution to the evolution of $\langle I_x \rangle$, and we recover Eq. (23). If the strength of the spin-locking field is increased to the point where $|\omega_1| \gg 1/\tau_h$, the toggling-frame master equation can be obtained by replacing Λ_1 with Λ_2 in Eq. (28), and resonator-induced relaxation of $\langle I_x \rangle$ is completely suppressed.

Section III B presents three simulations that characterize the effectiveness of nonideal spin locking in suppressing resonator-induced transverse relaxation. The Supplemental Material[25] includes simulations of relaxation during spin locking for 30 example systems consisting of three, four, or five hydrogen nuclei, with the dipolar Hamiltonian calculated using structures obtained from the Cambridge Structural Database (CSD).[26]

III. ANALYSIS AND SIMULATION OF EXAMPLE SYSTEMS

In this section we study the transverse relaxation of example systems in which the resonator is at temperature $T_h = 0$ K. The relaxation of two-spin systems during free evolution under the dipolar Hamiltonian and the chemical-shift Hamiltonians is analyzed in Sec. III A. In Sec. III B, the results of this analysis are used to gain a qualitative understanding of simulated relaxation in systems of a few spins. Simulations are performed in the interaction frame defined by Eq. (8), in which the coherent evolution associated with the spin Hamiltonian has been eliminated. In these simulations, dephasing makes no contribution to the decay of $\langle I_x \rangle$. A plotted value $\langle I_x \rangle(t)$ corresponds to what would be seen experimentally if a time reversal of all coherent evolution under the spin Hamiltonian could be performed at time t, with resonator-induced relaxation eliminated during the refocusing period. (The simulation methods are described in Sec. IV.)

A. Two-spin systems

If $H_{\rm spin} = 0$, the energy eigenstate of the two-spin system can be chosen as angular-momentum eigenstates:

$$|p\rangle \equiv |1,1\rangle, \quad |q\rangle \equiv |1,0\rangle, \quad |r\rangle \equiv |1,-1\rangle, \quad |s\rangle \equiv |0,0\rangle.$$

Here state $|I,M\rangle$ has angular momentum I and z component M. Since the Hamiltonian H_1 of Eq. (2) conserves spin angular momentum, the resonator cannot induce spin transitions between the $I = 1$ manifold and the $I = 0$ manifold. At 0 K, the only spin transitions that can occur are $|q\rangle \rightarrow |p\rangle$ and $|r\rangle \rightarrow |q\rangle$. Using the notation introduced in Eq. (18), we can write the rate constants for these transitions as

$$\Gamma_{q\rightarrow p} = \Gamma_{r\rightarrow q} = 2R_0, \tag{29}$$

where R_0 is given by Eq. (6). Comparison of Eq. (29) with Eq. (20b) shows that the spontaneous emission of states $|q\rangle$ and $|r\rangle$ is accelerated with respect to the spontaneous emission of a single spin, which is governed by the rate constant R_0.

Equation (19) can be used to write a relaxation equation for the hypothetical case where the rate of transverse relaxation is determined by the finite lifetimes of the states $|q\rangle$, $|r\rangle$:

$$\langle I_x \rangle = \frac{1}{\sqrt{2}}(\tilde{\rho}_{pq} + \tilde{\rho}_{qp}) \exp(-R_0 t) + \frac{1}{\sqrt{2}}(\tilde{\rho}_{qr} + \tilde{\rho}_{rq}) \exp(-2R_0 t). \tag{30}$$

[Notation has been simplified by replacing $\tilde{\rho}_{ij}(0)$ with $\tilde{\rho}_{ij}$.] By way of contrast, the relaxation equation for the system of isochronous, noninteracting spins is

$$\langle I_x \rangle = \frac{1}{\sqrt{2}}(\tilde{\rho}_{pq} + \tilde{\rho}_{qp}) \exp(-R_0 t) + \frac{1}{\sqrt{2}}(\tilde{\rho}_{qr} + \tilde{\rho}_{rq})[2\exp(-R_0 t) - \exp(-2R_0 t)]. \tag{31}$$

The differences between Eqs. (30) and (31) are due to spin transitions that convert $\tilde{\rho}_{qr}$, $\tilde{\rho}_{rq}$ into $\tilde{\rho}_{pq}$, $\tilde{\rho}_{qp}$, respectively. These transitions modify the spin order represented by the single-quantum coherences, rather than destroying it. As discussed in Sec. II C, transitions responsible for the reversible interconversion of coherences are associated with the terms $I_+ \rho I_-$ and $I_- \rho I_+$ in the relaxation superoperator of Eq. (5). When the resonator is at temperature 0 K, the spins cannot absorb quanta from the resonator, and so only the term $I_- \rho I_+$ contributes.

"Turning on" the homonuclear secular dipolar Hamiltonian H_D does not change the energy eigenstates or the rates at which spin transitions occur. However, H_D does introduce frequency shifts. In particular, the spectral peak at the Larmor frequency ω_0 is split into two peaks separated by $3\omega_{12}$, where ω_{12} is the secular dipolar coupling. This splitting is associated with a

frequency difference between the laboratory-frame coherences ρ_{qr} and ρ_{pq}, which appears in the interaction-frame master equation [Eq. (17)] as a modulation of the coupling between $\tilde{\rho}_{qr}$ and $\tilde{\rho}_{pq}$. Since the coupling constant is $2R_0$, the conversion of $\tilde{\rho}_{qr}$ to $\tilde{\rho}_{pq}$ will be averaged to zero by the dipolar coupling if

$$|3\omega_{12}|/2\pi \gg 2R_0.$$

Under these conditions, transverse relaxation is governed by Eq. (30), since all transitions dissipate the transverse spin. Note that an additional weak term $H' \ll H_D$ in the spin Hamiltonian cannot affect transverse relaxation. A weak perturbation cannot substantially change the eigenstates or the rates at which spin transitions occur, and small frequency shifts associated with H' cannot affect transverse relaxation, which is determined by the lifetimes of the spin states.

Unlike the dipolar Hamiltonian, a pure chemical-shift Hamiltonian slows the process of transverse relaxation. To understand the mechanism by which this occurs, we analyze the relaxation using a basis set composed of product states:

$$|1\rangle \equiv |{+}{+}\rangle, \quad |2\rangle \equiv |{+}{-}\rangle, \quad |3\rangle \equiv |{-}{+}\rangle, \quad |4\rangle \equiv |{-}{-}\rangle.$$

For the hypothetical case where the relaxation is determined by the lifetimes of the states $|2\rangle$, $|3\rangle$, and $|4\rangle$, the decay of $\langle I_x\rangle$ is biexponential, with decaying components that are governed by the rate constants $R_0/2$ and $3R_0/2$:

$$\begin{aligned}\langle I_x\rangle = {} & \tfrac{1}{2}(\tilde{\rho}_{12}+\tilde{\rho}_{21}+\tilde{\rho}_{13}+\tilde{\rho}_{31})\exp\left(-\tfrac{1}{2}R_0t\right) \\ & +\tfrac{1}{2}(\tilde{\rho}_{24}+\tilde{\rho}_{42}+\tilde{\rho}_{34}+\tilde{\rho}_{43})\exp\left(-\tfrac{3}{2}R_0t\right). \end{aligned} \quad (32)$$

Note that although the coherences listed in the second line of Eq. (32) are between states that differ by a single spin flip, these coherences decay more quickly than the coherences of a single-spin system. In the two-spin system, the lifetimes of product states $|a\rangle$, $|b\rangle$ are shortened by transitions involving either of the two spins, and the decay of certain coherences $\tilde{\rho}_{ab}$ is therefore faster than the decay of coherences in the single-spin system. It is reasonable to expect that a decrease in eigenstate lifetime with an increase in the number of spins is a typical feature of resonator-induced relaxation. As the number of spins is increased, the number of allowed transitions for a typical state is expected to increase, yielding a shortened lifetime. In this context, it should be noted that shortened eigenstate lifetimes do not necessarily correspond to an increased spin-polarization rate. If N spins are relaxing independently toward alignment with with the applied field,[14] for instance, with the relaxation of each spin governed by the rate constant R_0, then the lifetimes of product states will depend on N, whereas the polarization rate depends only on R_0.

In the system of two isochronous, noninteracting spins, the states $|2\rangle$ and $|3\rangle$ are degenerate, and the resonator can induce correlations between these two states, as discussed in Sec. II C. Since the interaction Hamiltonian H_1 conserves angular momentum, it induces transitions between correlated angular-momentum eigenstates, rather than between product states. These transitions, which modify the spin-spin correlations present in the system, can be considered to select particular linear combinations of degenerate states to participate in single-quantum coherences, namely, the states $|I=1,M\rangle$. The development of resonator-induced correlations can also be visualized as involving an indirect spin-spin interaction due to the coupling of many spins to a single resonator.[14]

A sufficiently large chemical-shift difference $\Delta\omega$ between the two spins will suppress the development of resonator-induced correlations, resulting in spontaneous emission by product states rather than correlated states. The chemical-shift Hamiltonian H_{CS} breaks the symmetry of angular-momentum conservation and modulates the indirect spin-spin interaction.[14] Within the formalism of the master equation, H_{CS} modulates the couplings between single-quantum coherences whose laboratory-frame frequencies differ by $\Delta\omega$. Define the sets $Z_1 = \{\tilde{\rho}_{13},\tilde{\rho}_{24}\}$ and $Z_2 = \{\tilde{\rho}_{12},\tilde{\rho}_{34}\}$, and note that the coherences in Z_i involve states differing by a flip of spin i. H_{CS} modulates the couplings between coherences that do not belong to the same set Z_i but has no effect on the couplings between coherences belonging to the same Z_i. Since the couplings between coherences in Z_1 and Z_2 all have magnitude $\leqslant R_0$, these couplings are averaged to zero if

$$|\Delta\omega|/2\pi \gg R_0. \quad (33)$$

As discussed in Sec. II C, resonator-induced correlations modify single-quantum coherences through the terms $[I_-I_+,\rho]_+$ and $[I_+I_-,\rho]_+$ in the relaxation superoperator. For the two-spin system, development of resonator-induced correlations is associated with the couplings between $\tilde{\rho}_{2k}$ and $\tilde{\rho}_{3k}$, where $k = 1,4$, as well as the couplings between $\tilde{\rho}_{k2}$ and $\tilde{\rho}_{k3}$. These couplings are suppressed when Eq. (33) holds, since they each involve one coherence in Z_1 and one in Z_2. Some couplings associated with the term $I_-\rho I_+$ are also suppressed by H_{CS} under these conditions; for example, the coupling between $\tilde{\rho}_{12}$ and $\tilde{\rho}_{24}$ is averaged to zero, since these coherences do not belong to the same set Z_i.

The chemical-shift Hamiltonian decouples the coherences in set Z_1 from those in Z_2, and so we can analyze separately the relaxation occurring within each set. Since the operators $I_+a^\dagger$, I_-a in the Hamiltonian H_1 each exchange a single quantum between the spins and the resonator, transitions between product states must be single-quantum transitions, involving the flip of only a single spin. Note that a flip of spin 2 simply interchanges the two coherences in set Z_1, and we might guess that the only transitions relevant for the relaxation within this set are those involving a flip of spin 1. Since the rate constants for flips of a single spin do not depend on the number of spins in the system,[14] we might further expect that the dissipation of the spin order represented by the coherences in Z_1 occurs at the same rate as for a single-spin system. It is simple to verify formally that this conclusion is correct, and that a similar conclusion holds for the coherences in Z_2. When Eq. (33) holds, transverse relaxation is exponential, and the time constant T_2 has the same value as in the case of an isolated spin $\frac{1}{2}$. The Appendix shows that this reasoning can be generalized to an N-spin system at arbitrary temperature. If a pure chemical-shift Hamiltonian decouples coherences involving a flip of spin i from those involving a flip of spin j, for all $i \neq j$, then transverse relaxation is exponential, and the time constant is

$$T_2 = 2/R_h,$$

where R_h is given by Eq. (11).

A weak dipolar coupling $H_D \ll H_{CS}$ that does not significantly perturb the eigenstates of the two-spin system can cause accelerated transverse relaxation. To first order, the effect of H_D is to introduce a frequency difference ω_{12} between the two coherences belonging to each set Z_i. If

$$|\omega_{12}|/2\pi \gg R_0,$$

then the reversible interconversion of coherences in the two-spin system is averaged to zero. The rate of transverse relaxation is then determined by the lifetimes of the energy eigenstates, and the relaxation is governed by Eq. (32).

It is interesting to compare the two regimes $H_D \gg H_{CS}$ and $H_D \ll H_{CS}$. In the first case, the frequency differences associated with H_D guarantee that all transitions cause dissipation of the transverse spin. Additional frequency shifts associated with a weak perturbation cannot affect transverse relaxation. In the second case, it is the first-order frequency shifts associated with the perturbation that are responsible for fast relaxation. We can expect these examples to be characteristic of larger systems. In cases where the dominant term in the spin Hamiltonian causes accelerated transverse relaxation, small frequency shifts associated with a weak perturbation cannot enable the reversible interconversion of coherences that would slow the relaxation process. If a spin Hamiltonian H' yields slow transverse relaxation, however, a weak perturbation H'' can cause accelerated relaxation by means of first-order frequency shifts that disrupt the reversible interconversion of coherences.

B. Systems of a few spins

For the characterization of resonator-induced relaxation in systems containing a few spins, 30 structures that contained carbon, nitrogen, oxygen, and either three, four, or five hydrogen atoms were randomly selected from the CSD.[26] The secular dipolar couplings[27] ω_{ij} between H nuclei were calculated for the selected structures, using the coordinates provided in the database. For each structure, we performed simulations using two Hamiltonians: H_D and $H_D + H_{CS}$. Rather than trying to estimate the anisotropic chemical shifts[27] for the H nuclei in each of these structures, we assigned chemical shifts randomly within a range of 0–10 ppm, in order to roughly characterize the way in which H_{CS} can affect transverse relaxation in systems of a few dipolar-coupled spins.[25] Relaxation during free evolution and during spin locking were both simulated. The field strength $\omega_1/2\pi =$ 50 kHz was chosen to illustrate nonideal spin locking. Efficient averaging of the resonator-induced transitions by the spin-locking field requires that the nutation of the spin system occur on a faster time scale than the evolution associated with the internal spin Hamiltonian, that is, $|\omega_1 I_x| \gg |H_{int}|$. Since some systems included dipolar couplings $|\omega_{ij}|/2\pi$ in the range of 25 to 30 kHz, departures from ideality were expected with a 50-kHz spin-locking field.

Adding chemical shifts to the dipolar-coupled systems did not yield qualitative changes in transverse relaxation during either free evolution or spin locking,[25] and so for simplicity we illustrate the results of the simulations using examples in which the spin Hamiltonian was H_D. In Figs. 2 through 4, the dash-dotted curves in red show transverse relaxation during free evolution, while the dashed curves in blue show relaxation of a spin-locked component. For purposes of comparison with these curves, the transverse relaxation corresponding to $H_{spin} = 0$ is shown as a dotted black curve, and the ideal case of exponential relaxation with time constant $2/R_0$ is shown as a solid black curve. As in the two-spin example analyzed in Sec. III A, "turning on" the dipolar Hamiltonian causes accelerated transverse relaxation during free evolution. The full set of relaxation plots shows a tendency toward faster relaxation during free evolution as the number of spins is increased,[25] and this tendency can also be seen in Figs. 2 through 4. Transverse relaxation is substantially slowed by spin locking, even in the case where the largest dipolar couplings $|\omega_{ij}|$ are within a factor of 2 of ω_1. Note that all structures for which spin locking showed large departures from ideality included dipolar couplings in the range of 20–30 kHz.

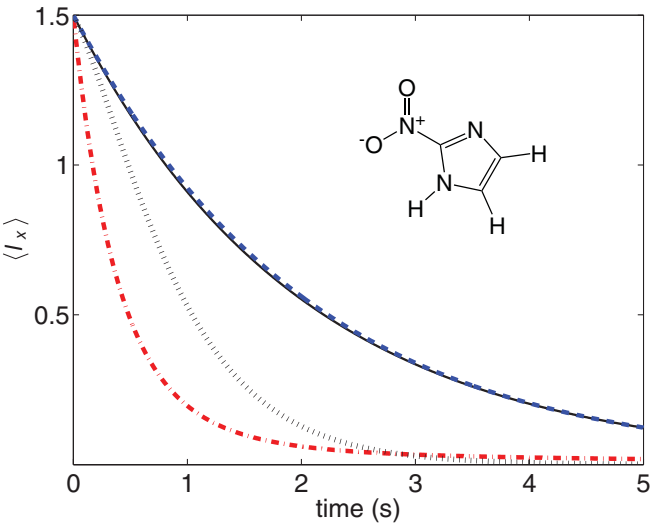

FIG. 2. (Color online) Transverse relaxation of a system of three dipolar-coupled H nuclei (CSD entry: celbaw) from an initial state aligned along the x axis. Two of the dipolar couplings $|\omega_{ij}|/2\pi$ are ∼4 kHz, while the third is ∼1 kHz. The dash-dotted curve (red) shows relaxation during free evolution, while the dashed curve (blue) shows relaxation during spin locking along the x axis, with $\omega_1/2\pi =$ 50 kHz. For purposes of comparison, the relaxation corresponding to $H_{spin} = 0$ is shown as a dotted black curve, and the ideal case of exponential relaxation with time constant $2/R_0 = 2$ s is shown as a solid black curve.

Figures 5 through 7 illustrate the way in which spin relaxation is modified by a pure chemical-shift Hamiltonian that assigns a distinct Larmor frequency to each spin. If the spacing between Larmor frequencies is sufficiently wide, both longitudinal[14] and transverse relaxation are exponential, and the respective time constants for the relaxation are $T_1 = 1/R_0$ and $T_2 = 2/R_0$. In Figs. 5 through 7, the dash-dotted curves in red show transverse relaxation, while the dashed curves in blue show longitudinal relaxation. The limiting cases of exponential relaxation, both longitudinal and transverse, are shown by solid black curves. The simulations in Fig. 6 show substantial oscillations about the exponential curves, due to the modulation of the indirect spin-spin interaction by H_{CS} (or, equivalently, due to the modulation of the couplings in the interaction-frame master equation). Since the Larmor

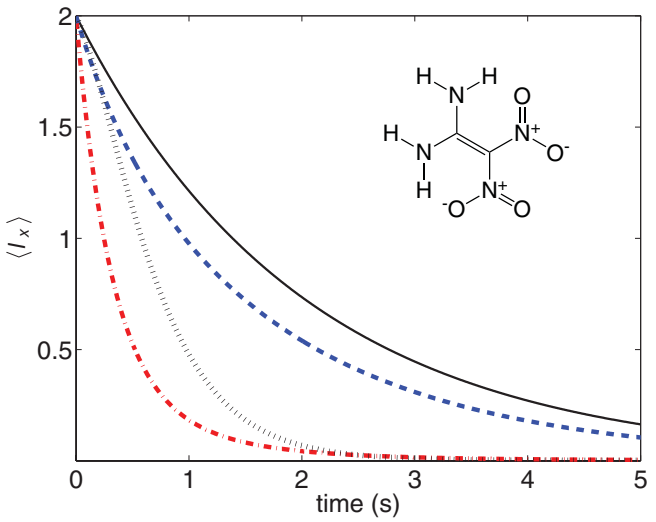

FIG. 3. (Color online) Transverse relaxation of a system of four dipolar-coupled H nuclei (CSD entry: sedtuq01). The two largest dipolar couplings $|\omega_{ij}|/2\pi$ are ∼26 kHz and ∼17 kHz. The curves are defined in the same way as in Fig. 2.

frequencies of the five spins are spaced in steps of only 1 Hz, resonator-induced correlations begin to develop within degenerate manifolds, but the slow modulation due to $H_{\rm CS}$ prevents these correlations from determining the time scale of the relaxation. In Fig. 7, a spacing of 3 Hz between Larmor frequencies allows for only small oscillations about the exponential curves.

Figure 8 shows how the exponential longitudinal and transverse relaxation in a system of fours spins with widely spaced Larmor frequencies are affected by a weak dipolar coupling $H_D \ll H_{\rm CS}$ that does not significantly perturb the eigenstates. Note first that the exponential longitudinal relaxation is not affected by the frequency shifts associated with the dipolar coupling. The strong chemical-shift Hamiltonian splits the

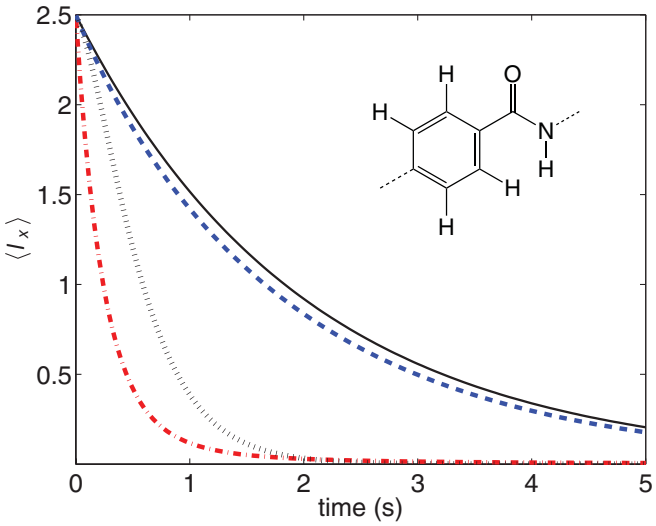

FIG. 4. (Color online) Transverse relaxation of a system of five dipolar-coupled H nuclei (CSD entry: wincur). The two largest dipolar couplings $|\omega_{ij}|/2\pi$ are ∼8 kHz. The curves are defined in the same way as in Fig. 2.

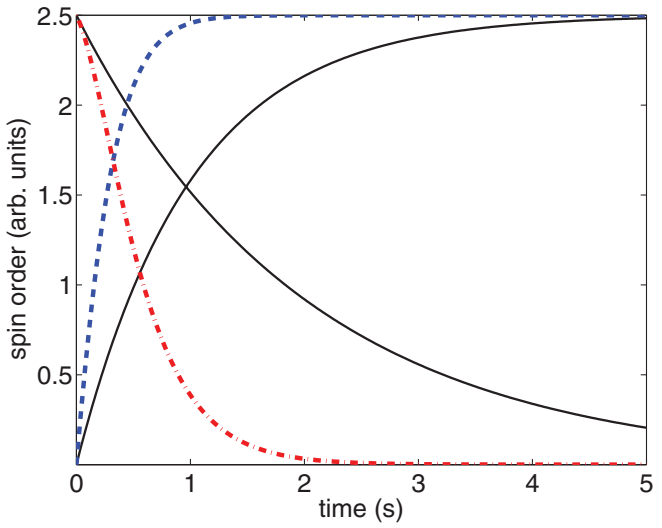

FIG. 5. (Color online) Longitudinal and transverse relaxation of five isochronous spins that interact only with the resonator. The spins are initially aligned along the x axis. The dashed (blue) and dash-dotted (red) curves show the respective evolution of $\langle I_z \rangle$ and $\langle I_x \rangle$. For purposes of comparison, the solid curve that starts at zero shows exponential longitudinal relaxation with time constant $T_1 = 1/R_0$, while the solid curve that decays toward zero shows exponential transverse relaxation with time constant $T_2 = 2/R_0$.

energy degeneracy of the product states, suppressing the development of resonator-induced correlations. Longitudinal relaxation then depends on independent spontaneous emission by individual spins, and the rate constant for this emission is not affected by frequency shifts.[14] However, the analysis in Sec. III A and in the Appendix shows that exponential transverse relaxation under $H_{\rm CS}$ depends on a reversible

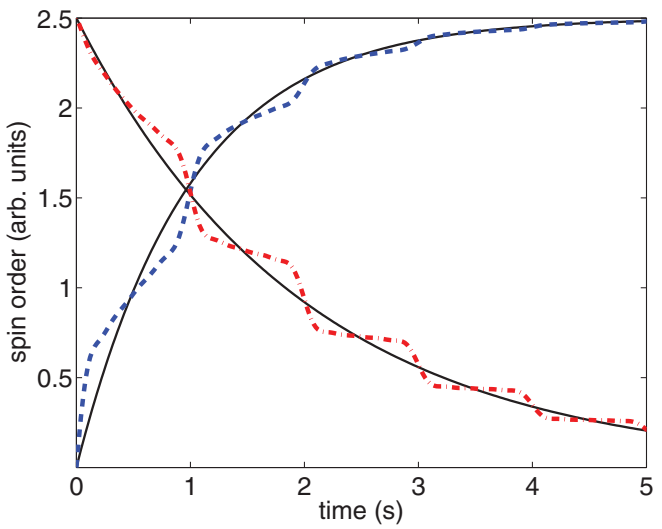

FIG. 6. (Color online) Adding chemical-shift offsets to the simulation of Fig. 5, with the Larmor frequencies of the five spins spaced in steps of 1 Hz, causes the couplings in the interaction-frame master equation to be modulated. Resonator-induced correlations begin to develop within degenerate manifolds, but the slow modulation due to $H_{\rm CS}$ prevents these correlations from determining the time scale of the relaxation.

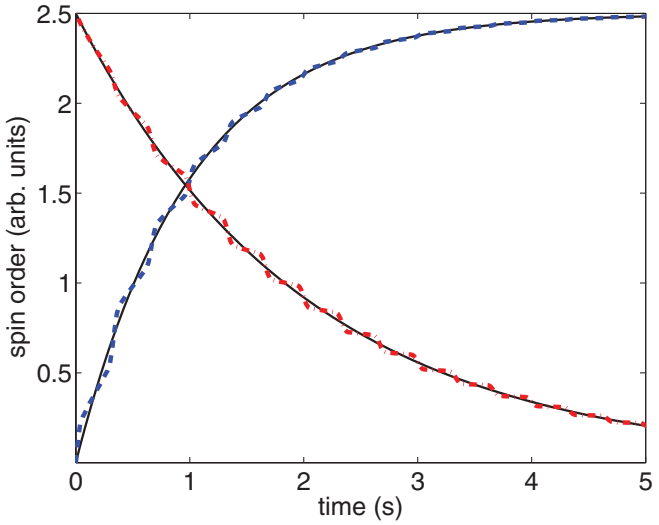

FIG. 7. (Color online) Adding chemical-shift offsets to the simulation of Fig. 5, with the Larmor frequencies of the five spins spaced in steps of 3 Hz, causes only small oscillations about the exponential curves.

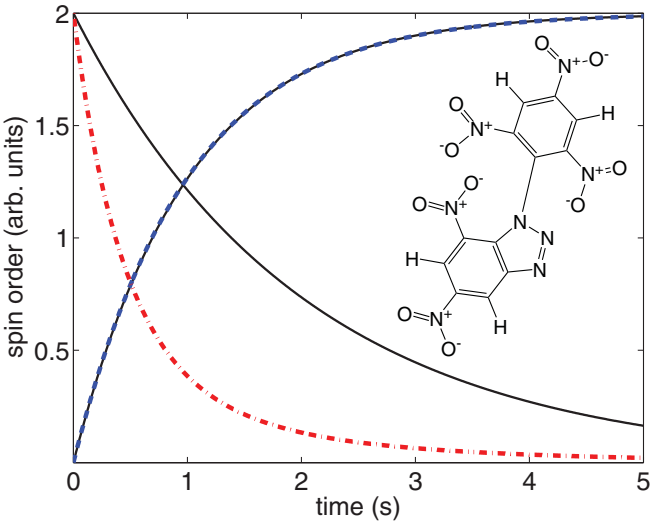

FIG. 8. (Color online) Longitudinal and transverse relaxation of four dipolar-coupled H nuclei (CSD entry: pabboj) from an initial state aligned along the x axis. The calculated dipolar couplings $|\omega_{ij}|/2\pi$ fell roughly between 50 and 100 Hz, aside from a single coupling ~250 Hz. To illustrate the relaxation occurring in the regime $H_D \ll H_{CS}$, chemical-shift offsets in steps of 1.2 kHz were assigned to the four spins, that is, the offset on spin j was $j \times 1.2$ kHz, where the spins were numbered according to the order in which they were listed in the database entry. (Note that these offsets correspond to steps of 2 ppm at a Larmor frequency of 600 MHz.) The dashed (blue) and dash-dotted (red) curves show the respective evolution of $\langle I_z \rangle$ and $\langle I_x \rangle$. For purposes of comparison, the solid curve that starts at zero shows longitudinal relaxation with time constant $T_1 = 1/R_0$, while the solid curve that decays toward zero shows transverse relaxation with time constant $T_2 = 2/R_0$.

interconversion of product-state coherences, and frequency shifts that average to zero the reversible transfers between coherences cause accelerated transverse relaxation. The spin transitions associated with these transfers then cause an irreversible loss of order, rather than a modification of the spin order. Figure 8 provides a striking illustration of the way in which frequency shifts can cause accelerated dissipation of a transverse nuclear-spin signal during free evolution, since the fast transverse relaxation is accompanied by slow longitudinal relaxation.

IV. SIMULATION METHODS

For all simulations presented in this paper, the rate constant for spontaneous emission by the spins into the resonant mode was $R_0 = 1\ \mathrm{s}^{-1}$, the Larmor frequency was 600 MHz, and the resonator temperature was 0 K. This value of R_0 is similar to that calculated for the resonator of Ref. 12, which has a mechanical frequency $\omega_h/2\pi \approx 600$ MHz. At this frequency, the mK temperatures achievable in a dilution refrigerator correspond to the low-temperature limit in which the spin polarization is of order unity and the thermal number of quanta in the resonator is $\ll 1$. For simplicity, a polarization of $P = 1$ was assumed; that is, the initial state had the spins aligned along the x axis. The simulations were performed in the interaction frame in which the coherent evolution associated with the spin Hamiltonian has been eliminated. Beginning from an initial density matrix $\rho(0)$, the interaction-frame evolution was calculated by first evolving the density matrix forward in time for a period t, with the forward evolution governed by Eq. (4), and then evolving $\rho(t)$ backward in time for the same period under the action of the spin Hamiltonian. The differential equation governing the backward evolution was thus obtained by setting the relaxation superoperator Λ to zero in Eq. (4):

$$\frac{d\rho}{dt} = -i[H_{\mathrm{spin}}, \rho].$$

These two evolution steps yielded

$$\tilde{\rho}(t) = \exp(itH_{\mathrm{spin}})\rho(t)\exp(-itH_{\mathrm{spin}}).$$

The evolution was simulated using the GAMMA library.[28] For simulations of spin locking, the nutation frequency about the applied rf field was $\omega_1/2\pi = 50$ kHz.

V. CONCLUSION

A strongly coupled resonator that allows for sensitive detection of nanoscale nuclear-spin samples can induce both longitudinal and transverse relaxation. In the low-temperature regime, where lattice fluctuations are "frozen out," fluctuating spin-resonator interactions can become the dominant source of relaxation, including spin cooling[14] and dissipation of spin-locked transverse signals.[12] The experimental observation of longitudinal relaxation induced by a microscale mechanical resonator in the high-temperature regime[18] suggests that resonator-induced transverse relaxation could be detectable under a variety of experimental conditions.

This paper has provided a theoretical description of resonator-induced transverse relaxation. A torsional resonator was used for purposes of visualization, but the analysis is not substantially altered if a translational mechanical resonator or an inductive resonator is coupled to the spins, since a similar formalism can be used to describe these systems.[14] In the

case where an isolated, freely precessing spin $\frac{1}{2}$ interacts with the resonator, both longitudinal and transverse relaxation are exponential, and the respective time constants for the relaxation are $T_1 = 1/R_h$ and $T_2 = 2/R_h$. The same conclusion holds for an N-spin system governed by a pure chemical-shift Hamiltonian $H_{\rm CS}$, provided the Larmor frequencies of the spins are distinct and sufficiently widely spaced. Although frequency shifts associated with a weak dipolar coupling $H_D \ll H_{\rm CS}$ do not affect longitudinal relaxation, they can cause accelerated transverse relaxation by averaging to zero the reversible interconversion of coherences. In a system of two isochronous spins that interact only with the resonator, transverse relaxation is accelerated by means of the same mechanism if a sufficiently strong dipolar Hamiltonian is "turned on." Simulations show that the dipolar Hamiltonian causes accelerated transverse relaxation in typical organic molecules containing a few H nuclei. More generally, the spin Hamiltonian can modify transverse relaxation through the following effects:

(1) changes in the structure of the spin-spin correlations present in the energy eigenstates, which affect the rates at which the states emit and absorb energy,[14]

(2) frequency shifts that modify emission and absorption rates within a degenerate manifold by splitting the energy degeneracy and thus suppressing the development of resonator-induced correlations within the manifold, and

(3) frequency shifts that introduce a difference between the oscillation frequencies of single-quantum coherences ρ_{ab} and ρ_{cd}, averaging to zero the transfers between them and thereby guaranteeing that the associated spin transitions cause irreversible loss of order.

Fast dissipation of the transverse signal is suppressed by spin locking strong enough to average the internal spin Hamiltonian $H_{\rm int}$. In the presence of a spin-locking field strong enough to average $H_{\rm int}$ but not the spin-resonator interactions occurring during the resonator's correlation time, relaxation of the spin-locked component is exponential with time constant $T_{1\rho} = 2/R_h$, the same time constant governing the transverse relaxation of a freely precessing spin $\frac{1}{2}$.

APPENDIX: EXPONENTIAL TRANSVERSE RELAXATION UNDER THE CHEMICAL-SHIFT HAMILTONIAN

Section III A analyzes a two-spin system in which a chemical-shift difference $\Delta\omega$ between spins 1 and 2 decouples product-state coherences involving a flip of spin 1 from those involving a flip of spin 2. If this chemical-shift difference is the only term in the rotating-frame spin Hamiltonian, transverse relaxation is exponential, and the time constant T_2 has the same value calculated for an isolated spin $\frac{1}{2}$. This result can be generalized to N-spin systems. Group the single-quantum product-state coherences into sets Z_k, where the coherences in set Z_k are between states which differ by a flip of spin k. We show here that if the resonator-induced transfers within each set Z_k are preserved, while transfers between coherences in Z_k and Z_j are suppressed for $k \neq j$, then the transverse relaxation during free evolution is exponential with time constant

$$T_2 = 2/R_h, \tag{A1}$$

the same value obtained for an isolated spin $\frac{1}{2}$ in Eq. (12). Alternately stated, the conditions for Eq. (A1) are that the Larmor frequencies of the N spins are distinct and sufficiently widely spaced, and that all product-state coherences involving a flip of spin k oscillate at the same frequency.

In demonstrating this result, we first define s_k to be the sum of the coherences within Z_k,

$$s_k = \sum_{\tilde{\rho}_{ab} \in Z_k} \tilde{\rho}_{ab},$$

and we claim that

$$\langle I_{kx} \rangle = \tfrac{1}{2} s_k. \tag{A2}$$

Equation (A2) can be established by expanding the density matrix as

$$\tilde{\rho} = \sum \tilde{\rho}_{ab} |a\rangle\langle b|,$$

and writing I_{kx} as

$$I_{kx} = \tfrac{1}{2}(I_{k+} + I_{k-}).$$

For each coherence $\tilde{\rho}_{ab}$ belonging to Z_k, we have

$$I_{k+}|a\rangle = |b\rangle, \quad I_{k-}|a\rangle = 0$$

or

$$I_{k+}|a\rangle = 0, \quad I_{k-}|a\rangle = |b\rangle.$$

Both cases yield

$$\mathrm{Tr}\,\{\tilde{\rho}_{ab} I_{kx}\, |a\rangle\, \langle b|\} = \tfrac{1}{2}\tilde{\rho}_{ab},$$

while for coherences $\tilde{\rho}_{cd}$ not belonging to Z_k, we have

$$I_{k+}|c\rangle \neq |d\rangle, \quad I_{k-}|c\rangle \neq |d\rangle,$$

which implies

$$\mathrm{Tr}\{\tilde{\rho}_{cd} I_{kx} |c\rangle\langle d|\} = 0.$$

Summing over the coherences in Z_k, we obtain Eq. (A2).

Since

$$\langle I_x \rangle = \sum_k \langle I_{kx} \rangle,$$

it suffices to show that

$$\frac{d}{dt} s_k = -\frac{1}{2} R_h s_k \tag{A3}$$

for arbitrary k. Two types of coupling constants in the master equation contribute to ds_k/dt: (1) the constants $\mathcal{R}_{abab}$, which cause the decay of $\tilde{\rho}_{ab}$; and (2) the constants $\mathcal{R}_{cdab}$, responsible for the interconversion of coherences within Z_k. From Eq. (19), $\mathcal{R}_{abab}$ is given by

$$\mathcal{R}_{abab} = -\frac{1}{2}\left(\sum_{n\neq a} \Gamma_{a\to n} + \sum_{n\neq b} \Gamma_{b\to n}\right).$$

The rate constants $\Gamma_{m\to n}$ for transfer of population between product states which differ by a single spin flip are the same as for the two states of a single-spin system,[14] and it follows that

$$\mathcal{R}_{abab} = -\frac{1}{2} R_h - \frac{1}{2}\left(\sum_{n\neq a,b} \Gamma_{a\to n} + \sum_{n\neq b,a} \Gamma_{b\to n}\right). \tag{A4}$$

We show that the interconversion of coherences in Z_k compensates for the decay associated with the term in parentheses on the right side of Eq. (A4).

The coupling constants $\mathcal{R}_{cdab}$ are associated with the terms $I_+\rho I_-$ and $I_-\rho I_+$ in the relaxation superoperator of Eq. (5). Transfer from $\tilde{\rho}_{ab}$ to $\tilde{\rho}_{cd}$ involves two transitions $|a\rangle \rightarrow |c\rangle$ and $|b\rangle \rightarrow |d\rangle$, with both transitions involving a flip of spin $j \neq k$ in the same direction. We first consider the case where both transitions involve an upward flip of spin j:

$$I_{j+}|a\rangle = |c\rangle, \quad I_{j+}|b\rangle = |d\rangle.$$

Equation (5) can be used to evaluate $\mathcal{R}_{cdab}$:

$$\mathcal{R}_{cdab} = R_0(n_{\rm th}+1) = \tfrac{1}{2}(\Gamma_{a\rightarrow c}+\Gamma_{b\rightarrow d}).$$

Similarly, in the case where both transitions involve a downward flip,

$$\mathcal{R}_{cdab} = R_0 n_{\rm th} = \tfrac{1}{2}(\Gamma_{a\rightarrow c}+\Gamma_{b\rightarrow d}).$$

The nonzero rate constants $\Gamma_{a\rightarrow n}$, $\Gamma_{b\rightarrow n}$ appearing in Eq. (A4) can be grouped into pairs $(\Gamma_{a\rightarrow c},\Gamma_{b\rightarrow d})$ such that there is a one-to-one correspondence between these pairs and the coherences $\tilde{\rho}_{cd}$ in Z_k that are coupled to $\tilde{\rho}_{ab}$. It follows that Eq. (A4) can be written as

$$\mathcal{R}_{ababa}\tilde{\rho}_{ab} = -\frac{1}{2}R_h\tilde{\rho}_{ab} - \sum \mathcal{R}_{cdab}\tilde{\rho}_{ab}, \qquad \text{(A5)}$$

where the sum is over the coherences $\tilde{\rho}_{cd}$ in Z_k that are coupled to $\tilde{\rho}_{ab}$. Equation (A5) can be interpreted to mean that the decay governed by the coefficient $\mathcal{R}_{ababa}$ of the master equation includes a contribution associated with dissipation, for which the rate constant is $R_h/2$, and a contribution associated with transfers from $\tilde{\rho}_{ab}$ to other coherences in Z_k. If we sum the derivatives of all coherences in Z_k, terms of the form $\pm\mathcal{R}_{cdab}\tilde{\rho}_{ab}$ cancel, leaving only terms of the form $-(R_h/2)\tilde{\rho}_{ab}$. It follows that Eq. (A3) holds, and we conclude that resonator-induced transverse relaxation is exponential with time constant $T_2 = 2/R_h$.

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